MIXED MATRIX VANADIUM OXIDE CATALYTIC NANOCOMPOSITE MEMBRANE FOR STYRENE OXIDATION

by

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Behnam Koohestani

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LIST OF ABBREVIATIONS

α -Al_2O_3	Alfa-alumina
□-Al_2O_3	Gama-alumina
AFM	Atomic Force Microscopic
ANOVA	Analysis of variance
AlOOH	Boehmite
AAO	Porous anodic aluminum oxide
BET	Nitrogen adsorption analysis
Bza	Benzaldehyde
Bzac	Benzoic acid
CNT	Carbon nanotubes
CMR	Catalytic membrane reactor
CVD	Chemical vapor deposition
CNT/V_xO_y	Carbon nanotube/vanadium oxide
DOE	Design of experiment
EDX	Energy Dispersive X-ray
FT-IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectroscopy
H_4NO_3V	Ammouium metavanadate
h	Hours
min	Minutes
MWCNTs	Multi wall carbon nano tube
NT	Nano tube

PEG	Polyethylene glycol
PVA	Polyvinyl alcohol
Pha	Phenylacetaldehyde
PPM	Porous polymeric material
PVP	Polyvinylpyrrolidone
PEI	Polyethylenimine
Phed	1-phenylethane-1,2-diol
RSM	Response surface methodology
SO	Styrene oxide
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TIVO	Triisopropoxy vanadium
TGA	Thermal gravimetric analysis
TEOS	Tetraethoxysilane
TMOS	Tetramethoxysilane
VOC	Volatile organic carbon
TS-1	Titanium silicalite-1
X_xO_y	Vanadium oxide ($VO, V_2O_3, V_2O_5, V_6O_{13}$)
$V_xO_y/ \square Al_2O_3$	Vanadium oxide impregnated $\square Al_2O_3$
V_xO_y-NTS	Vanadium oxide nanotubes
V_xO_y/ CNT	Vanadium oxide impregnated CNT
XRD	X-ray Diffractometer
1D	One-dimensional

LIST OF SYMBOLS

Symbols	Descriptions	Unit
r_{st}	rate of reaction	mol/(L h)
τ	time	h
A	pre exponential factor	
t	time	h
T	absolute temperature	K°
S	catalyst surface area	m^2
X_{st}	styrene conversion to benzaldehyde	
X_{st0}	initial styrene conversion to benzaldehyde	
$X_{oxidant0}$	initial oxidant conversion to benzaldehyde	
M	molar ratio of oxidant (H_2O_2) and styrene	
k_0	specific rate of reaction	L/(mol h)
k_s	overall rate constant	L/(mol h)
$C_{oxidant0}$	initial oxidant (H_2O_2) concentration	mol/L
C_{st0}	initial styrene concentration	mol/L
EA	activation energy	cal/(mol K)
e	Error	
l	Thickness of coating	m
p	product	
R^2	Coefficient of determination	
E	Activation energy	cal/mol
R	gas constant	
V_{pore}	pore volume	m^3
V_{mem}	membrane volume	m^3
□	membrane porosity	
F	Solution Flux	$lm^{-2}h^{-1}$

MEMBRAN PEMANGKIN KOMPOSIT NANO VANADIUM OKSIDA SECARA MATRIKS BERCAMPUR UNTUK PENGOKSIDAAN STIRENA

ABSTRAK

Pengoksidaan sebatian olefin kepada epoksida atau oksida setara dengan menggunakan pemangkin logam oksida adalah satu langkah penting dalam pembuatan bahan kimia gred tinggi dan farmaseutikal dalam kuantiti yang besar. Penggunaan vanadium oksida sebagai pemangkin logam oksida mendapat perhatian khusus disebabkan keadaan pengoksidaannya dari +2 hingga +5 dan kepelbagaian sifat kimia stereo dengan julat koordinasi dari empat hingga lapan; menjadikannya logam oksida yang menarik dalam pengoksidaan olefin.

Struktur nano tersusun logam oksida seperti pertumbuhan logam oksida pada dinding tiub karbon nano (CNTs) adalah menarik dalam pemangkinan disebabkan luas permukaan tentu yang tinggi dan sifat-sifat uniknya. CNT terbenam vanadium oksida dijangka menghasilkan bahan komposit baru dengan sifat-sifat fizikal dan ciri-ciri pemangkin yang dipertingkatkan.

Kememilihan tertingkat dalam tindak balas pengoksidaan boleh dicapai melalui pemangkin matriks bercampur dan reka bentuk reaktor. Penggunaan reaktor membran bermangkin memudahkan persentuhan bahan-bahan tindak balas dalam fasa cecair. Dalam kerja ini, satu lapisan nipis membran bermangkin V_xO_y-CNT/γ-Al_2O_3 (~ 1 μm) telah disediakan dan dipantau dalam keupayaan pengoksidaan stirena. Logam oksida nanokomposit V_xO_y/CNT disediakan dengan kaedah pembentungan basah, kemudiannya diurai dalam sol AlOOH. Selepas itu, ia disalut pada permukaan penyokong menggunakan kaedah sol-gel. Faktor-faktor yang mempengaruhi penyediaan salutan tanpa kecacatan seperti jenis pengikat, masa untuk menambah pengikat ke dalam sol dan rawatan permukaan penyokong telah

dikaji. Membran tiada penyokong dan berpenyokong telah dicirikan dengan menggunakan teknik-teknik seperti SEM, TEM , FTIR, TGA, AFM, XRD dan penjerapan-penyahjerapan nitrogen.

Reka bentuk eksperimen (DOE) digunakan untuk mengoptimumkan pengoksidaan stirena dan kememilihan benzaldehid. Bagi membran pemangkin, keadaan pengoksidaan optimum boleh dicapai pada suhu tindak balas 45 □C, perbezaan tekanan separa 1.5 bar, nisbah mol H_2O_2/stirena 1.5:1 dan beban pemangkin 30%; di mana penukaran maksimum stirena 25.6% dan kememilihan benzaldehid 84.9%. Manakala keadaan optimum dengan pemangkin nanokomposit V_xO_y /□-Al_2O_3 dicapai pada suhu tindak balas 62.74 □C, dalam tempoh 5.15 j, nisbah mol H_2O_2/stirena 2.7:1 dan beban pemangkin 0.34 g; di mana penukaran maksimum stirena 68.23% dan kememilihan benzaldehid setinggi 57.32%.

Ia adalah jelas bahawa pengoksidaan stirena boleh diperbaiki dengan menggunakan pemangkin komposit berasaskan vanadium oksida dengan menggunakan H_2O_2 kering sebagai agen pengoksidaan. Jenis pemangkin, struktur pemangkin dan keadaan tindak balas mempunyai pengaruh yang kuat ke atas pengoksidaan stirena. Tiub nano vanadium oksida yang disintesis melalui kaedah hidroterma mempunyai prestasi yang rendah akibat kemusnahan pengoksidaan. Walau bagaimanapun, kelemahan ini boleh diatasi dengan menggunakan CNTs sebagai acuan. Produk utama pengoksidaan stirena adalah benzaldehid. Dengan menggunakan V_xO_y-CNT/□-Al_2O_3 sebagai membran pemangkin, penukaran stirena berkurangan tetapi kememilihan benzaldehid meningkat berbanding dengan serbuk nanokomposit disebabkan oleh pencegahan tindak balas sampingan. Membran boleh menghalang tindak balas sampingan dengan mengasingkan produk dari bertindak balas selanjutnya dengan H_2O_2.

MIXED MATRIX VANADIUM OXIDE CATALYTIC NANOCOMPOSITE MEMBRANE FOR STYRENE OXIDATION

ABSTRACT

The oxidation of olefin compounds to equivalent epoxides or oxides using metal oxides as catalyst is an important step in the manufacturing of large quantities of fine and pharmaceutical grade chemicals. The chemical property of vanadium as metal in its oxide state is of interest particularly in application during dilute oxidation. Well-defined metal oxide nanostructures on the walls of carbon nanotubes (CNTs) are attractive as catalyst in the oxidation reaction because of their high specific surface area and formation of novel composite material with enhanced physical and catalytic properties. In this work, a thin layer of V_xO_y-CNT/γ-Al_2O_3 catalytic membrane (about 1 μm) was prepared and observed for its styrene oxidation capability. Metal oxide nanocomposite V_xO_y/CNT was prepared by wet impregnation method dispersed in sol, AlOOH. It was then coated on the surface of support through sol-gel technique. Factors that affect the preparation of defect free coating such as type of binder, time for the addition of binder to sol and surface treatment of the support, were investigated. The physical and chemical properties of the unsupported and supported membrane were characterized using different techniques such as SEM, TEM, FTIR, TGA, AFM, XRD and nitrogen adsorption-desorption.

Design of experiments (DOE) was applied to optimize the styrene oxidation conversion and benzaldehyde selectivity using the prepared membrane and nanocomposite catalyst. The optimal oxidation conditions were achieved at reaction temperature of 45 °C, partial pressure difference of 1.5 bar, molar ratio of H_2O_2/styrene of 1.5:1 and loading of 30 wt. % catalyst on membrane. These

conditions resulted in maximum styrene conversion of 25.6% and benzaldehyde selectivity of 84.9%. In the case of nanocomposite catalyst (V_xO_y/γ-Al_2O_3), optimum oxidation conditions were reaction temperature of 62.74 °C, time of 5.15 h, molar ratio of H_2O_2/styrene of 2.7:1 and catalyst loading of 0.34 g for maximal styrene conversion of 68.23% and maximum benzaldehyde selectivity of 57.32%.

The results showed that styrene oxidation was improved using vanadium oxide-based composite catalysts with anhydrous H_2O_2 as an oxidant. Vanadium oxide nanotube, synthesized through hydrothermal technique also has relatively poor performance due to the oxidative degradation of template. However, using CNTs as a template, the shortcoming of vanadium oxide nanotube was overcome. Thus, using V_xO_y-CNT/γ-Al_2O_3 as catalytic membrane decreased styrene conversion and increased benzaldehyde selectivity (main product of styrene oxidation). This showed effectiveness of membrane to prevent side reaction, and isolate the product from further reaction with H_2O_2.

CHAPTER 1

INTRODUCTION

1.1 Membrane Technology

Today, membrane processes are at the centre of resolve and settlement of many important industrial problems, such as water treatment and desalination, food and beverages, pharmaceutical and medical applications, gas separation, full cell, biochemical reactions and catalytic reactions (Mulder, 1996).

Membranes are barriers, permeable to one or more species in a mixture, which separate two distinct zones and create a driving force for components to move from one zone to the other. Even though systematic studies of membrane phenomena may be traced as early as 18^{th} century, but not much of development was found until 20^{th} century. The first commercially significant gas separation membranes were introduced only in 1979, but within 10 years a wide range of different types of gas separation membranes have been developed (Noble and Stern, 1995). Moreover, membranes found their first considerable application in the filtration of drinking water at the end of World War II. By 1960, the fundamentals of modern membrane science had been developed, however membranes were used in only a few laboratories and small, specialized industrial applications (Mark, 2004). About thirty years ago, membrane filtration was not economically feasible, because of the disability of precisely controlling the pore size and pore morphology and also the specific materials that were used to produce the membrane, were restricted, but now this problem is settled and membrane technology has been further developed.

The two most important, and often the most expensive chemical process are usually the chemical reaction and the separation of the product stream. Both the

process could be improved by the combination of these two operations into a single unit operation, leading to potential savings in energy and reactant consumption and reduced by-product formation (Strathmann, 2001). One promising way to accomplish this combination is the use of membrane separation and catalytic reaction together in a multifunctional reactor.

The idea of catalytic membrane was first suggested by Sun in 1987 (Sun and Khang, 2002) thereafter, Burggraf (Burggraaf, 1989) indicated that the modification of □-alumina membrane as catalytic membrane is possible. Over the past two decades, interest in membranes as a functional component of a reactor has significantly increased (Aran et al., 2011; Caro et al., 2010; Felice et al., 2010; Julbe et al., 2001; Klose, 2004; Rodri□guez et al., 2011; Takehira et al., 2004). Catalytic membrane reactor (CMR) is currently a challenging research subject in the field of membrane science and catalytic reaction engineering. Catalytic membrane reactor is one of the different membrane reactor configurations that are interesting because it could concurrently carry out two major operations: reaction and separation (Hsieh, 1991).

1.2 Application of Catalyst to Homogeneous and Heterogeneous Reactions

Catalysts are used in approximately 90% of chemical, petrochemical and material manufacturing, so it is necessary to produce catalytic materials that are efficient, reusable over many cycles, and suitable for a wide range of processes (Maurya et al., 2011a). Catalysts do not change the thermodynamics of reaction, but slightly alter the kinetics of the reaction by providing an alternative pathway between the initial and final state of chemical reaction.

As shown in Figure 1.1, energy barrier is lowered with the introduction of catalyst in the process resulting in a more complex pathway of reactions. Therefore, catalyst increases the reaction rate constant, k by decreasing the activation energy, E as given in the Arrhenius relationship $k= Ae^{-E/RT}$.

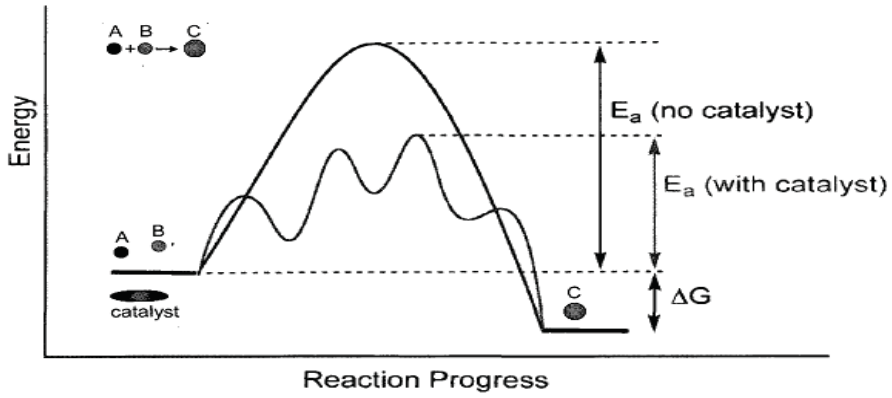


Figure1.1: Effect of catalyst on a chemical reaction

Catalysts are commonly classified as enzymatic, homogeneous and heterogeneous (Swiegers, 2008). Homogeneous catalysts are located in the same phase as the reactants, and involve the reactions taking place on a single active site. They are often comprised of single molecule. On the other hand, heterogeneous catalysts are solids, generally in the form of supported transition metals, which catalyze reactions of molecules in liquid or gaseous phases. As a result, heterogeneous catalysis takes place at an interface between a gas or liquid and a solid surface, where many different types of active sites like single atom or a group of atoms may be involved in the reaction. This might lead to a large number of products in spite of the fact that only one group might be desirable.

1.3 Nanoparticles Catalysis

The discovery of carbon nanotube (CNT) (Iijima, 1991) led to determining a unique structure for novel products, in addition to their physical properties and interesting shapes. There are several reports published on comprehensive development in synthetic routes and structure of nano-scaled materials and application of nano materials since 1991 (Ajayan, 1999; Cevc and Vierl, 2009).The synthesis of different kinds of inorganic nanomaterials was the motivation for chemists, physicists and material researchers to focus their attention toward the design of a variety of tubular or other types of structures containing nanoparticles (Jana et al., 2001; Shenton et al., 1999; Tremel, 1999).

The functionality of a heterogeneous catalyst depends critically on its structure over a length scales (Goodwin, 2004).Metal nanoparticles were likely observed over 2500 years ago (Daniel and Astruc, 2003). However, in the last 20 years, the study of nanoparticles has increased dramatically due to their unique size and properties. The interest for study and using nanoscale material is especially apparent in the field of catalysis because metal and metal oxide nanoparticles often show increases activity compared with their bulk metal counterparts (Okatsu et al., 2009; Polshettiwar et al., 2009). In heterogeneous catalysts, the favorable form of catalysts, are typically been stabilized or immobilized on different type of supporting material that will be discussed in detail as follow (Ishida et al., 2008).

1.4 Common Nanoparticle Supports

The efficient catalyst supports must have high surface areas to facilitate loading of the catalyst. In this section we discuss the various types of nanoparticle supports.

1.4.1 Metal Oxide Supports

Metal oxides are one of the most extensively employed catalyst supports since they offer high thermal and chemical stability. While they are in the form of zeolites, they as well have a well-defined pore structure and a high surface area. The surfaces of metal oxides can be simply functionalized, to simplify the procedure for catalyst deposition. The most common metal oxides used as catalyst supports are silica, alumina, titania, ceria, and zirconia.

Silica is normally used in catalytic reactions that require mild temperatures, < 300 °C, because at higher temperatures, it is less stable and can produce volatile hydroxides. Alumina offers higher thermal and mechanical stability than silica, thus mainly used as metal oxide support. Alumina exists in a number of forms, but the two most common are □-alumina and □-alumina. □-Alumina is a highly porous, amorphous material that offers surface areas as high as 300 m^2/g and pore sizes as small as 5 nm, on the other hand, □-alumina is a nonporous, crystalline solid that has a relatively low surface area (3-5 m^2/g). □-alumina is highly stable even at temperatures as high as 1200 ^oC (Chorkendorff, 2003).

Silica and alumina are characteristically classified as inert materials, compared to other metal oxide supports such as titania, ceria, and zirconia which show reactive properties in certain reactions (Boaro, 2009; Han, 2009).

1.4.2 Carbonaceous Supports

Carbon materials offer a multiplicity of advantages as catalyst supports. Some carbon supports have surface areas as high as 1500 m^2/g and pore sizes less than 1 nm, but graphitic carbon has a moderately low surface area. Much of the present research with carbon supported catalysts focuses on developing novel carbon

materials such as carbon nanotubes as catalyst supports (Satishkumar et al., 2000) Carbon nanotubes are unique substrates for catalyst immobilization because of their high surface area, unique physical properties and morphology, and high electrical conductivity. Additionally, their small size and hollow geometry facilitates the formation of small nanoparticles (typically 1 - 4 nm), which is ideal for catalysis.

1.4.3 Polymer Supports

As an option to conventional metal oxides and carbon, polymeric materials are attractive as nanoparticle supports because of their adaptability. Many polymeric materials contain heteroatom that can form complexes with metal nanoparticles, and the flexible structure of the polymers often makes them principally effective at stabilizing metal nanoparticles and preventing aggregation. Also, the variety of functional groups available in polymeric materials is almost unlimited. Some of the most common types of polymers used for nanoparticle immobilization include water soluble polyelectrolytes such as polyvinylpyrrolidone (PVP) and polyethylenimine (PEI) (Sun and Wang, 2003; Tsunoyama et al., 2008; Tsunoyama et al., 2005), polymeric microspheres (Liu, 2006), and ion exchange resins (Ishida, 2007; Shi, 2005).

1.4.4 Porous membranes as catalyst supports

As mentioned above, high surface areas result from a highly porous structure with comparatively small pore sizes, however small pores often exhibit high mass transport resistances during the catalytic reaction. Porous membranes, which can consist of virtually any ceramic or polymer material, offer a support configuration that provide several advantages over the conventional catalyst supports (Armor, 1995). One of the motivations for using membranes as catalyst supports is the ability

to catalyze reactions and perform separations at the same time. Also, membrane reactions can run continuously because the catalyst does not need to be separated from the reaction products, unlike batch and stirred tank reactors. The internal pores of the membrane also provide a large surface area that permits a high loading of the catalytic material.

1.5 Membranes Reactors

Common membrane materials can be separated into two main classes, polymeric (organic) and inorganic. The main limitations of polymeric membranes are their low operating temperatures and chemical stability. Inorganic membranes can operate at higher temperatures and are typically more chemically resistant. Table 1.1 lists a number of membrane materials (polymeric and inorganic) along with their maximum operating temperature and the suitable pH range. Inorganic membranes are generally more resistant to organic solvents and corrosive chemicals than the organic membranes, and are more suitable for use in most reaction systems due to their higher thermal and chemical stability.

The application of membranes in chemical reactors is motivated mostly by the synergy effect that is created by the preferential permeation of products (or reactants), leading to higher conversion and/or selectivity, and a potentially reduced downstream separation load. There has been an intense, worldwide effort on membrane reactors research since the 1980ِ and these efforts have been summarized in a number of recent review articles (Andric et al., 2010; Basile et al., 2006; Fong et al., 2008; Giorno and Drioli, 2000; Li et al., 2009; Mozia, 2009; Shu et al., 1991; Westermann and Melin, 2009).

Table 1.1: Operating limits and restrictions for various membrane materials (Hsieh, 1996)

Material	Maximum Operating Temperature (^{o}C)	pH Range
Cellulose acetate	50	3-7
Aromatic polyamides	60-80	3-11
Fluorocarbon polymers	130-150	1-14
Polyimides	140	2-8
Nylons	150-180	*na
Polycarbonate	60-70	*na
Polyvinyl chloride	120-140	*na
Alumina	>900	0-14
Glass	700	1-9
Zirconia	400	1-14
Silver	370	1-14
Stainless steel(316)	>400	4-11

*na= not available

Depending on the configuration of membrane reactors, they may provide a number of other advantages as well. Catalytic membranes are typically divided into four categories: retainment of homogeneous catalysts, extractors, distributors, and contactors, which are discussed below in detail.

1.5.1 Retainment of Homogeneous Catalysts

Thermal recovery of homogeneous catalysts is regularly uneconomical due to low concentrations and can lead to deactivation of the catalyst. Retention of a homogeneous catalyst or precious smaller ligands, allowing the permeation of the residual reaction mixture could be achieved using membrane reactor as shown in Figure1.2. Membrane bioreactor for example, is particularly popular in bio catalytic applications (Giorno and Drioli, 2000; Westermann and Melin, 2009) and can be either realized by immobilizing the catalyst on the membrane surface or by a membrane filtration with a dissolved or dispersed catalyst.

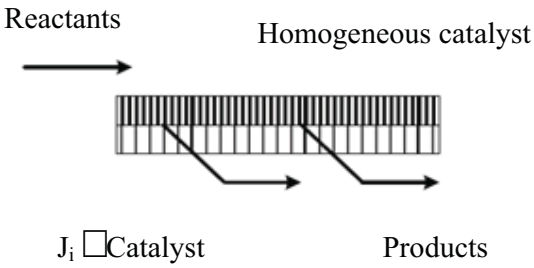


Figure 1.2: Retainment of homogeneous catalysts (Seidel-Morgenstern, 2010a)

1.5.2 Membrane Reactors for the Preferential Removal of a Species (Membrane Extractors)

The function of a membrane extractor is to selectively remove a product from the reaction mixture.In the late 1960ي; researchers began to exploit the excellent separation capabilities of membranes for catalytic applications. The earliest work in this area employed membrane extractors to remove one or more of the products from the reaction to shift the equilibrium and increase its conversion. If the reaction is equilibrium-limited, the decreased activity of the species being removed will permit further conversion to occur, beyond that which would be possible if no species were removed. When reactions are limited by equilibrium, the membrane can continuously and selectively remove the product to shift the equilibrium.

Many of the initial studies with membrane extractors involved beneficial hydrogen removal in reactions such as hydrocarbon dehydrogenation (Collins et al., 1996; Hجllein et al., 2001), water gas shift (Criscuoli et al., 2001), and methane steam reforming reactions (Shu et al., 1994). Figure 1.3 shows a membrane reactor that preferentially removes a species from an equilibrium limited reaction and hence improving the reaction conversion.

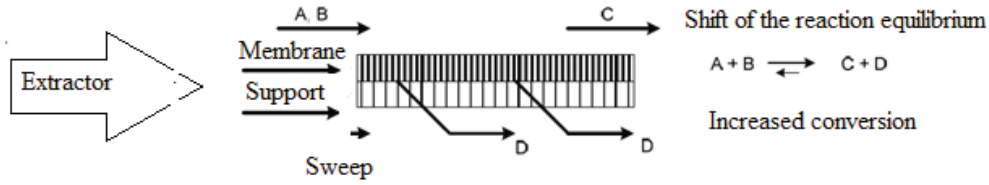


Figure 1.3: Extractor Membrane(Seidel-Morgenstern, 2010a)

1.5.3 Membrane Reactor for Distributed Addition of a Reactant (Membrane Distributors)

The idea of a distributed reactant feed is useful to systems with two competing reactions. A typical example is the partial oxidation of a hydrocarbon. Distributor membrane reactors present controlled addition of a reactant to the reaction mixture to limit side reactions and provide higher selectivity for the desired product. This may happen by simply controlling the amount of a reactant that is introduced on one side of the membrane, or by selectively allowing one component from a mixture to pass through the membrane and undergo reaction.

Figure 1.4 demonstrates the reaction of two components, A and B, to yield a product, C without the continued formation of D. As component B permeates through the membrane, it reacts with component A on the other side of the membrane to form product C. The reaction of B creates a concentration gradient within the membrane, which is the driving force for the continued permeation of B and subsequent reaction with A. Because B reacts with A immediately upon permeating through the membrane, very little side reactions occur to produce D. This principle is complicated by the change in residence time behavior of the reactants as one of them is fed gradually (Klose et al., 2003).The most common example of this type of reaction is the partial oxidation of hydrocarbons (K$_{\xi}$lsch et al., 2002). In these reactions, O_2 reacts more easily with the partially oxidized species than the

starting material. By controlling the addition of O_2 (B) to the hydrocarbon stream (A), complete oxidation can be limited.

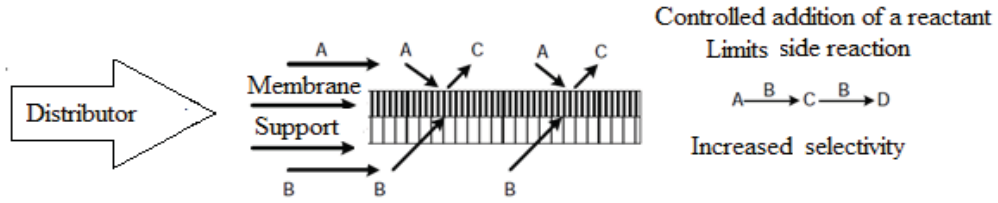
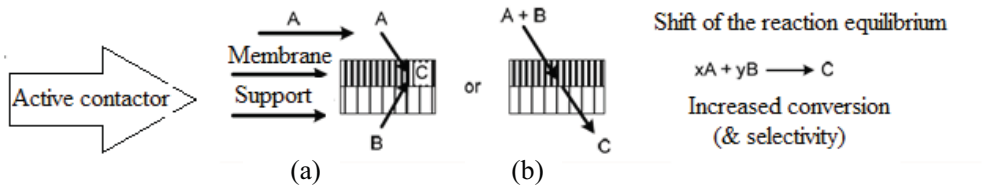


Figure 1.4: Membrane reactors for distributed addition of a reactant (Seidel-Morgenstern, 2010)

1.5.4 Membrane Reactors for Control of Reactant Contact (Membrane Contactors)

The newest form of catalytic membrane reactor is the membrane contactor, where the membrane acts as a support that brings the reactants into contact with the catalyst. In the case of extractors and distributors, the membrane is often catalytically inert and simply acts as a support with a fixed bed of catalyst on one side of the membrane. In that case, the membrane is solely responsible for the separation step, while the fixed catalyst bed is responsible for the reaction. Membrane contactors typically have catalyst deposited within the membrane pores, making them catalytically active, but they usually do not perform a separation function. Although, they do not fulfil the requirements for catalytic membrane reactors in the traditional sense (combining separation and reaction), most researchers in the field still characterize them as a form of catalytic membrane reactor. Membrane contactors are further classified into two categories in which the membrane acts as an interface between multiple phases (Figure 1.5 a) or the membrane is utilized for dead-end flow

where all the reactants pass through the catalytically active membrane pores (Figure 1.5 b) (Miachon et al., 2003).



Figur 1.5: Membrane reactors for control of reactant contact (Seidel-Morgenstern, 2010a)

1.5.4 (a) Interfacial Contactors

Interfacial contactors, which are also known as catalytic diffusers, exploit the membrane as a catalyst support to facilitate contact between reactants that are in multiple phases. The membrane could cause enhanced contact between the catalyst and the reactants. The common application for interfacial contactors is gas/liquid contacting for reactions such as hydrogenations or oxidations.

A gas/liquid contactor typically has the gas on the side of the membrane that has larger pores and the liquid on the side that contains more of the catalyst, which is usually the skin layer. The gas and liquid solutes then diffuse to the catalyst surface and react. Flow of the liquid and gas facilitates transport of reactants and removal of products from the reaction zone. This configuration was successfully applied to oxidize organic acids to CO_2 and H_2O (Miachon et al., 2003) and short chain alkanes to oxygenates (Espro et al., 2001). A number of studies had been carried out for hydrogenation of unsaturated substrates including cinnemaldehyde (Pan et al., 2000), methylenecyclohexane and sunflower seed oil (Bottino et al., 2002) with excellent success, in some cases achieving high selectivity for the desired product. There has

also been significant interest in using interfacial contactors for removal of nitrates from drinking water by hydrogenation (Reif and Dittmeyer, 2003).

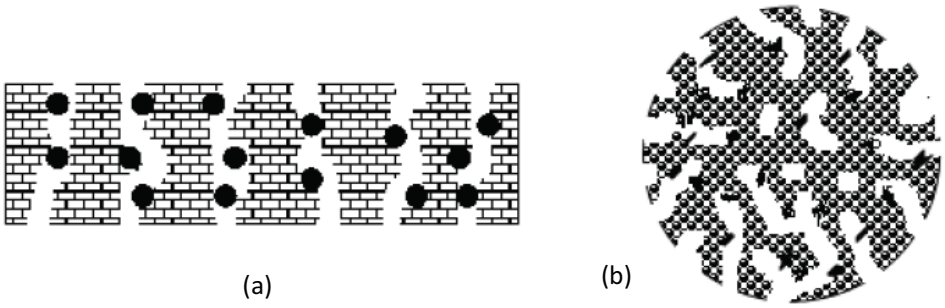
The interfacial contactor configuration is also beneficial for forming contact between two liquid phases. The reactants diffuse into the pores from each side of the membrane and come into contact at the catalyst surface.

1.5.4(b) Flow-Through Contactors

Membranes operated as flow-through contactors act similarly to conventional fixed bed reactors. In traditional fixed bed reactors, the reactants need to diffuse into the pores of the support to react with the catalyst, but in flow through membrane contactors, convective mass transport rapidly brings the reactants to the active surface of the immobilized catalyst (Figure 1.6). If the pores are adequately small, radial diffusion will not limit reactions even at high flow rates where the contact time is very short. In this way, the pores of the membrane act as microreactors in which the reaction conversion can be controlled by simply adjusting the flow rate (Westermann and Melin, 2009). Flow-through contactors also have the advantage of constantly removing the products from the reaction zone. As a result, there will be less competition between products and reactants for active sites on the catalyst and a decreased possibility for the products to undergo side reactions or poison the catalyst surface.

The flow-through contactor configuration allows fine control over the residence time of reactants inside the membrane, which directly affects conversion. Even a single pass through the membrane yields nearly complete conversion in reactions such as volatile organic carbon (VOC) combustion or photocatalytic oxidation of organic compounds. However, a majority of previous experiments with

flow-through contactors passed the reactant mixture through the membrane multiple times to obtain complete conversion. Many of these studies focused on gas-phase hydrogenation or oxidation reactions (Kormann et al., 2004).



Fgure 1.6: Schematic diagram showing the flow of reactants through a membrane operated as a (a) flow-through contactor, and around a catalyst bead from a (b) traditional fixed bed reactor.

The flow of gaseous mixture through the membrane very rapidly allows very short contact time, which results in partial hydrogenation of compounds such as acetylene, propyne, butadiene, and hexadiene (Groschel et al., 2005; Lambert and Gonzalez, 1999; Lange et al., 1998; Pelzer et al., 2003). The flow-through configuration is also beneficial for gas/liquid reactions where a limited amount of gas is able to dissolve in the liquid phase. Thus with each pass, the liquid solution can again be re-saturated with the gas. Schmidt and co-workers found that this strategy afforded high selectivity in the partial hydrogenation of a number of unsaturated organic compounds including cyclo-octadiene, 1-octyne, phenyl acetylene, and geraniol (Schmidt et al., 2005; Schmidt et al., 2008). Others had similar success with partial hydrogenation of sunflower oil (Bengtson and Fritsch, 2006; Fritsch and Bengtson, 2006; Schmidt et al., 2008) and a-methylstyrene (Purnama et al., 2006) and hydrogenation of nitrate for water denitrification (Ilinich et al., 2003; Reif and

Dittmeyer, 2003). The overall success of membrane reactors in restricting the extent of reaction could make them quite valuable in a number of applications.

1.6 Benzaldehyde Synthesis and Application

Benzaldehyde C_6H_5CHO, is the simplest and the most industrially useful member of the family of aromatic aldehydes. Benzaldehyde exists in nature, primarily in combined forms such as glycoside in almond, apricot, cherry, and peach seeds. The characteristic benzaldehyde odor from oil of bitter almond occurs because of trace amounts of free benzadehyde formed by hydrolysis of the glycoside amygdalin. Amygdalin was □rst isolated in 1830 from the seeds of the bitter almond.

The only industrially important processes for the manufacturing of synthetic benzaldehyde involve the hydrolysis of benzalchloride and the air oxidation of toluene. The hydrolysis of benzalchloride, which is produced by the side-chain chlorination of toluene, is the older of the two processes. It is not utilized in the United States in Europe, India, and China. Other processes, including the oxidation of benzylalcohol, the reduction of benzoylchloride, and the reaction of carbon monoxide and benzene, have been utilized in the past, but they no longer have any industrial application(kirk-Othmer, 1999).

The air oxidation of toluene is the source of the majority of the world□s synthetic benzaldehyde. Both vapor and liquid-phase air oxidation processes have been used. In the vapor phase process, a mixture of air and toluene vapor is passed over a catalyst consisting of the oxides of uranium, molybdenum, or related metals. High temperatures and short contact times are essential to maximize yields. Small amounts of copper oxide may be added to the catalyst mixture to reduce formation of by-product maleic anhydride. Conversion per pass is reported to be low, 10□20%,

with equally low yields, 30-50%. The vapor-phase oxidation of toluene was the dominant process in the 1950s and early 1960s, but is now of little industrial importance, thus paving way for the liquid-phase process. In the liquid phase process, both benzaldehyde and benzoic acid are recovered. This process was introduced and developed in the late 1950s by the Dow Chemical Company, as a part of their toluene-to-phenol process, and by Snia Viscosa for their toluene-to-caprolactam process (kirk-Othmer, 1999). The benzaldehyde recovered from the liquid-phase air oxidation of toluene may be purified by either batch or continuous distillation.

1.7 Problem Statement

□-Al_2O_3 has been widely studied for preparation and modification of catalytic membranes using the sol-gel method because these types of membranes can be used for oxidation reaction purposes (Alfonso et al., 2000; Bottino et al., 2005b). □-Al_2O_3 membranes are typically supported on macro porous □-Al_2O_3 tubes or disks in the sol-gel method; they are dip or spin coated with a boehmite (AlOOH) precursor to improve conversion or selectivity (Xia et al., 1996).

However, when AlOOH is applied, the surface on which □-Al_2O_3 is catalytically embedded must be free of cracks after calcination. Therefore, choosing a suitable binder that can be burned off in the calcination step without negative side effects on the catalyst or membrane is important. Although catalytic membranes with different shapes, catalyst loadings and binders have been prepared and tested in commercial ceramic support structures (Alfonso et al., 1999; Alfonso et al., 2002; Teixeira et al., 2011), to the best of our knowledge, no studies on the use of vanadium oxide (V_xO_y) supported on multi-walled carbon nanotubes (CNTs) or

vanadium oxide NTs for styrene oxidation in catalytic membranes have been investigated. The reason is because no suitable and effective catalyst has been developed for this purpose.

The large surface area 1315 m^2/g for SWNTs, outstanding thermal conductivity (3000W/□K m) and chemical and mechanical stabilities of CNTs, make them promising for the development of advanced composite materials that undergo catalytic oxidation reactions (Chen et al., 2007b). As a result of their amazing properties, CNTs have been introduced into many host materials, including polymers, metals and ceramics, to improve the overall properties of CNT composite systems (Sharma et al., 2010; Thostenson et al., 2001).

The growth of metal oxides on the walls of carbon nanotubes (CNTs) is a common technique for preparing composite materials (Neri et al., 2010). The use of vanadium oxide nano-structures as metal oxide catalysts is of particular importance because vanadium oxides can be used for the partial oxidation or dehydrogenation of alkanes to olefins (Ledoux et al., 2001; Weckhuysen and Keller, 2003a; Xu et al., 2002). Therefore, blends of vanadium oxides and CNTs are expected to produce novel composite materials with enhanced chemical and physical properties (Chen et al., 2007b).

Embedding carbon nanotubes and vanadium oxides into □-Al_2O_3 poses several critical challenges that must be overcome to capture the full potential of CNT composites. The uniform dispersion of CNTs in the host matrix material is essential. As a result of van der Waals forces, CNTs are likely to form agglomerates or bundles instead of individual tubes, and this can produce defects in composite membranes. The second main challenge is associated with strengthening the interaction between

CNTs and the host matrix to produce stable composite materials that are capable for the styrene oxidation at relatively short time.

The oxidation of olefin compounds to equivalent epoxides or oxides is an important step in the manufacturing of large quatities of fine- and pharmaceutical-grade chemicals (Lutz, 1980). For example, the oxidation of terminal alkenes, such as styrenes, is difficult and necessitates longer reaction times (Coperet et al., 1997). Styrene oxide and benzaldehyde are typically manufactured by oxidizing styrene, with stoichiometric amounts of peracids as the oxidizing agent (Swern, 1971). Styrene oxidation in the presence of H_2O_2 is widely used in the production of two significant products, Styrene oxide and benzaldehyde (Al-Ajlouni et al., 2008; Hulea and Dumitriu, 2004b; Selvaraj et al., 2008; Wang et al., 2005). To the best of the authors' knowledge, no studies on benzaldehyde production with V_xO_y-CNT as the catalyst and V_xO_y-CNT/ □-Al_2O_3 as the catalytic membrane have been investigated.

The selective oxidation of styrene is particularly difficult, because it is a kinetically rapid reaction, so it is of great importance to control the reaction to avoid side reactions. The purpose of this study is to investigate the use of a short contact time reactor in order to maximize production selectivity and protected from producing side reaction products. In particular, maximizing the concentration of benzeldehyde from styrene and restricting the formation of by product is important industrially. To do this, □- Al_2O_3 pellet was dip coated in V_xO_y /CNT bohemite solution to form a gel and then calcined to form a thin layer of V_xO_y /CNT /□-Al_2O_3 catalyst. A mixture of styrene/H_2O_2/acetone was fed and the conversion and benzaldehyde selectivity results were measured.

From the above discussion, it was found that benzaldehyde has many industrial applications as listed above. It can be produced via styrene oxidation. Styrene oxidation generates many side reactions which lead to large amount of by products. Also, the reaction takes a long time to reach completion using powder catalyst. In most studies, styrene oxidation requires temperature over and above 60 ^{o}C and more importantly is the production of environmentally unfriendly substances from the usage of peroxy acid such as tetra butyl hydrogen peroxide or other oxidants which are corrosive and hazardous.

Therefore, to overcome these challenges, catalytic membrane was developed as alternative to powder catalyst which can produce benzaldehyde as well as separates the products during reaction through the membrane. It can be inferred in this study that the developed catalyst performs dual function (enhancement of the reaction and separation). Secondly, H_2O_2 as an oxidant, though has been applied in other processes, but there is no information about the use of H_2O_2 as oxidant in catalytic membrane to produce styrene oxide and benzaldehyde. Above all, energy required during the reaction was successfully reduced by lowering the temperature to 40 ^{o}C which clearly showed the activity and efficiency of the developed catalytic membrane.

1.8 Research Objectives

The present research has the following objectives:

1- To develop and synthesize vanadium oxide nano structure composite catalyst and mixed matrix nanocomposite membrane

2- To characterize the developed nanostructure composite catalyst and mixed matrix nanocomposite membrane with suitable analytical techniques

3- To investigate the performance of nanostructure composite catalyst and catalytic membrane for styrene oxidation and obtain an optimum operating conditions for the reaction

4- To study the reaction kinetics of styrene oxidation

1.9 Scope of the Study

In this study, the main objective is to develop a suitable vanadium oxide base catalytic membrane for styrene oxidation to benzaldehyde. For this purpose, different shape of vanadium oxide base nanoparticle catalyst and Mixed Matrix catalytic membrane were tested.

The overview of research activities carried out as following:

1.9.1 Synthesis and Characterization of Nanocomposite Catalyst

Different types of nanostructure catalyst were synthesized by hydrothermal and impregnation methods. Hydrothermal method was applied for preparation of vanadium oxide nanotube from vanadium pentoxide and hexadecylamine precursor. Aluminum tri-sec-butoxide (Al $(C_3H_7O)_8$), MWCNTs and NH_4VO_3 were used for impregnation method and synthesis of V_xO_y /CNT and V_xO_y /□-Al_2O_3. The catalysts were characterized using XRD, SEM, TEM, FT-IR, TGA and Nitrogen adsorption-desorption.

1.9.2 Synthesis and Characterization of Mixed Matrix Vanadium oxide Catalytic Nanocomposite Membrane

Mixed matrix vanadium oxide catalytic nanocomposite membrane was synthesized using sol-gel method. Three type of nanocomposite catalyst (1) V_xO_y /CNT, (2) VO_x-NTs, (3) nanoparticle size V_xO_y/γ-Al_2O_3 were first add inside sol alumina then membrane were synthesized using dip coating method and sol-gel process. The membranes were characterized using XRD, SEM, TEM, FT-IR, TGA, Nitrogen adsorption-desorption, AFM and EDX.

1.9.3 Design and Fabrication of Liquid Permeation Membrane Test Rig

A liquid permeation test rig was designed and fabricated for determining the performance of disc type membrane. The test rig was designed for styrene oxidation reaction with H_2O_2 as oxidant using mixed matrix vanadium oxide catalytic nanocomposite membrane at different operating conditions. The operating parameters that can be adjusted using this test rig include feed flow rate, gas flow rate, temperature and vacuum sweep gas pressure.

1.9.4 Kinetic Study

A simple kinetic study for the oxidation reaction of styrene using nanocomposite catalyst and mixed matrix nanocomposite membrane was studied to obtain its kinetic model and the activation energy was calculated using Arrhenius equation. This was done in order to obtain parameters for the purpose of reactor design in commercialization.

1.10 Organization of the Thesis

The thesis consists of five chapters as listed in table of contents. A brief introduction on catalyst, membrane and catalytic membrane technology are included in chapter 1 (Introduction). At the end of this chapter, problem statements that provide basis and rationale to justify the research direction in the current study are highlighted. Based on the problem statement; the specific objectives of the research are together with the research scope.

Chapter 2 (Literature Review) presents literature review on the oxidation of hydrocarbon and styrene oxide with different types of catalyst, oxidation of hydrocarbon with vanadium base catalyst, application of catalytic membrane for oxidation of hydrocarbon. The recent developments for synthesis CNT, functionalization of CNT, vanadium oxide nano tube, are presented.

Chapter 3 (Materials and Methods) presents the detail of materials and chemicals used in the present study. This is followed by the detailed experimental procedures, which include the membrane preparation method, characterization methods and analytical techniques. The synthesis method for membrane support and sol-gel derived catalytic membrane is discussed in detail, which includes the preparation of catalytic nanocomposite template. The characterization method for membrane physicochemical properties such as thermogravimetric behavior, type of interatomic bond, crystalline phase and porous structure are also outlined in chapter3. Details of the experimental set up are also elaborated in this chapter.

Chapter 4 (Results and Discussion) is the core of this thesis, which address the five objectives as listed in chapter1. The results of the experimental are sub-divided into six sections. The first section presented the characterization of nanocomposite catalyst. This is followed by the performance of nanocomposite in

styrene oxidation. Design of Experiment (DOE) approach is applied to determine the optimum operation process variables. The third section presented the characterization of membranes. This is followed by the performance of membrane in styrene oxidation base on Design of Experiment (DOE) for determination of optimum operation process variable. In the final section, the simple kinetic study for styrene oxidation based on different kind of nanocomposite catalyst and catalytic membrane are presented.

Chapter five (Conclusions and Recommendations) concludes all the major finding obtained in the present study. At the end of the thesis, suggestion and recommendations to improve the present research work as well as the future direction of the research are presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrocarbons

Today there are more than 30,000 specialty chemicals produced industrially from approximately 300 intermediate chemicals (Moulijn, 2001). The enormous majority of these intermediates are produced from an extremely limited number of approximately 20 simple base chemicals for example, ethylene, butane, ammonia, methanol, propylene, sulfuric acid and chlorine.

Hydrocarbons are an integral part of our global economy and are utilized as fuels, commodity chemicals, specialty chemicals, intermediates and final product. Production of most hydrocarbons begins with the refining of petroleum followed by further treatment in petrochemical plants to produce the desired hydrocarbon product. Functionalizing hydrocarbons broadens their uses to include fuels, polymers, specialty and commodity chemicals, and various other industries. Oxygenated products are a valuable part of these hydrocarbon derived products and their production relies heavily on catalytic selective oxidation reactions (Cavani and Trifiر 1997; Grasselli, 2002; Grasselli et al., 2003).

In spite of the long history of chemical reaction engineering there are still many problems which are not solved in an acceptable manner (Levenspiel, 1999). This problem lies in the fact that during the synthesis of a certain target component usually undesired parallel or consecutive reactions occur which reduce the achievable yields. Therefore, there is considerable interest in developing technologies which allow increasing the selectivity and yield with which a certain target product can be generated. It is well known that the selectivity in reaction networks towards a target compound can be increased following various concepts.

First, a careful selection of the reaction temperature can be made to favor the formation of the target. Second, applying dedicated catalysts which accelerate specifically the desired reaction (Ertl, 2008). The third approach, exploits the fact that the selectivity with respect to a certain preferred product can be increased by properly adjusting the local concentrations of the reactants involved (Seidel-Morgenstern, 2010b).

2.2 Selective Oxidation of Hydrocarbons

The addition of oxygen to hydrocarbons is the simplest method to functionalize a hydrocarbon. Oxidation of hydrocarbons to alcohols, aldehydes, epoxide and acids comprise the largest category of catalytic organic reactions and almost all monomers in manufacturing are obtained by catalytic oxidation processes (Haber, 1996). Oxidation reactions in the chemical sector are made much more selective in nature by means of a catalyst which lowers the activation energy for the selected process and produces the useful products. Figure 2.1 shows the important industrial organic chemicals produced by heterogeneous oxidation.

Oxidation processes present a significant challenge as the selective oxidation reactions struggle with the combustion reactions. Haber has identified the following as the most important factors in the selective oxidation of hydrocarbons (Haber et al., 1992):

1. Thermodynamics favour the formation of water and carbon dioxide in hydrocarbon oxidation, consequently kinetic control of the reaction is required for the formation of partial oxidation products.
2. Hydrocarbon-oxygen mixtures facilitate multiple series and parallel reaction pathways to occur and then the catalyst must control the relative rates of each